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A Thesis

Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
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INTRODUCTION

Magnesium and magnesium alloys are becoming more and more important in modern industry. Their use in the aviation industry has been greatly curtailed because of their comparatively poor resistance to corrosion especially in moist atmospheres. Many methods have been adopted to improve their resistance to corrosion. Various paints and laquers have been used but no entirely satisfactory results have been obtained. In search of a better protective coating investigators have recently attempted the electrocoating of magnesium.

Various methods for electrocoating magnesium and magnesium alloys have been mentioned in patented literature but experimental evaluation of these methods shows that probably none would be commercially successful.

(1) W. S. Loose has recently developed a method of depositing adherent nickel plates on magnesium alloys. The process consists of a series of steps inwhich the metal is first etched slightly in a chromic-nitric-sulphuric acid bath, then treated in a hydrofluoric-nitric acid solution to deposit a fluoride film prior to being plated with nickel from a nickel bromoflouride bath. The effect of concentration of the various constituents both in the pretreating and

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(1) W. S. Loose, preprint 81-6. Electrochemical Society.

in the plating baths is discussed. Both nickel fluoride and bromofluoride plating baths have been studied extensively as to the effect of concentration, current density, pH and temperature on the type of the deposits produced. The deposits obtained on magnesium are soft, adherent, and easily buffed to a high luster. They withstand indoor and dry atmospheres very well, but they are not recommended for moist, corrosive conditions due to the corrosion of the magnesium produced by the nickel magnesium couple through porosity in the deposits.

In order to get an effective coating on magnesium the ideal element would be one which would be anodic to magnesium. Such an element under a corrosive condition would go into solution in preference to magnesium, thereby affording a sacrificial coating to magnesium.

There has not been a great deal of work done on the determination of electropotentials of the more active metals. Magnesium is one of the more active metals and is more electronegative than any of the common metals. Nickel has a standard potentials of -0.231 volts compared to a potential of -1.866 volts for magnesium. Magnesium is therefore anodic to nickel in aqueous solutions and goes into solution in preference to nickel. Generally speaking the greater the contact potential the faster the corrosion takes place when in contact with water. On the basis of this, then, it is only logical to assume that the ideal electrocoating would be a metal which lies above magnesium on the electro-

chemical series. If we examine the series in search of this metal we find only a few that are in this group, namely, Li, Rb, Ca, Na, and Be. Of these we can eliminate all but beryllium because of their extreme reactivity even at room temperatures.

Beryllium is one-third lighter than aluminum and considerably more rigid than steel and possesses a remarkable resistance to corrosion. It is with this last property that we are primarily concerned.

(2) Plating beryllium on metals into which it can defuse can be done much below the melting point of beryllium. Between 550 and 580 degrees centigrade beryllium can be plated on aluminum in a black layer which gives aluminum a superficial hardness.

According to M. Merlub - Sobel,(3) the Kemet laboratories Inc., of Cleveland have developed a process using another salt and electroplating at a lower temperature.

An investigation on the electrodeposition of beryllium on magnesium would require equipment which was not available at the Montana School of Mines. However, the use of beryllium in this capacity apparently offers excellent possibilities.

Since we have eliminated the metals that are anodic

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(2) Thompson: Theoritical and applied electrochemistry. 1939 Ed. p. 446

(3) M. Merlub-Sobel, Trans. Am. Electrochemical Soc. 54, 65 (1928)

to magnesium, the next step is to examine the metals that are immediately below magnesium in the electrochemical series.

Aluminum lies just below magnesium. Like beryllium plating any investigation concerning aluminum plating would require special equipment because of the high temperatures involved and although there are some possibilities in this field the work could not be performed in the metallurgy laboratory under the present conditions.

Manganese is the next fairly common metal that is encountered on the electromotive series and it can be passed with only one comment. That is, the metal does not protect itself well enough to be considered as a useful material in protecting another metal. Besides protecting the metal or alloy that the element is plated upon the electrodeposition must have the ability to protect itself.

The next common metal in the electrochemical series is zinc. Zinc is a common covering for the protection of iron but it has not been widely used as a protective coating for other metals.

According to the electrochemical series of the elements that has been referred to in this work zinc is cathodic to magnesium by approximately 1.10 volts. This however would only be true under certain conditions of solution concentration, and temperature. Under different conditions the electromotive force might not be nearly as great. This point is well illustrated by some actual tests conducted by the Aluminum Company of America.(4)

(4) Mazlo-Magnesium Alloys 1943 (p.14)

In a sodium chloride solution the potential of zinc was found to be slightly more negative than all of the common aluminum alloys and only slightly less negative than the magnesium and magnesium alloys. On the basis of this, then, although zinc will probably not give a sacrificial coating to magnesium, it would be well worth while to endeavor to produce a continuous coating of electrolytic zinc on magnesium and conduct corrosion tests if the experiment is successful.

This problem, "Zinc Plating Magnesium", was undertaken with the hope that some light might be thrown on the answer to the question of how to improve the corrosive resistance of magnesium and magnesium alloys.

APPARATUS

The accompanying diagram (Fig. 1.) shows the setup used for all the experimental work.

The direct current was furnished by a type B1 21L rectifier manfactured by the B-L Electric Mfg. Co. for the Central Scientific Co. It was connected to an alternating current line of 115 volts and sixty cycles. The rectifier had a power consumption of 35 Watts. Six volts and two amperes of direct current are produced.

A 0.0 to 2.8 ohms variable resistance rheostat was connected in series in order to give variable current densities.

A model 280 Weston ammeter was connected in series, and a model 280 Weston voltmeter was connected in parallel across the electrolytic cell.

To keep the solution well agitated a two winged stirring rod was used in a variable speed agitator (Type A 0 6 0-7) manufactured for the Central Scientific Company of Chicago, Ill.

A hand operated breaker switch was also used.

EXPERIMENTAL WORK

Zinc has been successfully plated on aluminum from a modified zinc cyanide bath. Since no literature could be found on zinc plating magnesium and since magnesium and aluminum have similar physical and chemical properties, it was decided that this bath would be used as a basis for the preliminary laboratory investigation.

The magnesium electrodes were prepared from a rod of cast magnesium of high purity. About three inches of the rod was cut off and then this piece was cut in two equal sections with a hack saw. The face of the electrodes was then buffed and polished to a high luster.

The surface was then rinsed in hot water and dried.

(5) The preplating steps used were the same as those recommended for aluminum and consisted of the following:

I. Cleaning Solution.

$NaCO_3$.....18 grams per liter

$Ca_3(PO_4)_2$.....20 " " "

Temp. .....85°C.

II. Rinse in cold water.

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(5) Thompson, Theoretical and Applied Electrochem. P. 201

III. Dip in a 4 per cent HF acid solution

60 seconds.

IV. Rinse in cold water

The zinc plating bath consisted of the following:

NaCN.....53.2 g. /L.

$Zn(CN)_2$.....59.2 g. /L.

NaOH.....43.8 g. /L.

Na_2CO_3..... 9.5 g. /L.

$Al_2(SO_4)$ ..... 4.7 g. /L.

Cur. Den. ..... 2 amp. /sq. dm.

Temp. ..... 40°C

Anode ..... Lead

Moderate Stirring

pH..... 10.9

The first deposit was produced under the above conditions.

The immersion of the magnesium in the bath resulted in a continuous evolution of hydrogen and a loose layer of basic magnesium oxide and zinc was continually sloughed off by the hydrogen. The zinc deposited was in the form of a spongy black metal with no adhesion to the magnesium.

Other tests were made with current densities varying from one ampere per square decimeter to 15 amperes per square decimeter but the deposits were essentially the same. Likewise variations in temperature of the bath also had no

noticable effect on the character of the deposit. Glue and sodium acetate used as addition agents, separately and together, had no effect on the deposit. From these results it was evident that this bath was not suitable and therefore did not warrant any further investigation.

BATH II.

The conventional cyanide zinc plating bath as described by Blum and Hogabloom[5] was the second bath used. The composition of this bath is as follows:

$Zn(CN)_2$	.....	60 g/liter
Na (CN)	.....	23 " "
Na (OH)	.....	53 " "
Temperature	40 - 50°Centigrade	
Current Density	(1-2 amp. /sq. dm.)	
Cathode Current Efficiency	...	90 - 95%
Anode	.....	Pb.

The solution composition of this bath was maintained within (±) 10% and the ratio of M total sodium cyanide to zinc ion was within the allowable range of 2 - 2.5 as recommended by Hull and Wernlund.[6]

The preplating procedure described on page 7 is used for this deposit.

The first deposit was run at a cathode current density of 1.0 amp/ dm^2 at a temperature of 40° C. A continuous zinc

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(5) Principals of Electroplating and Electroforming, 2nd. Ed.(1930)

(6) Modern Electroplating 1942 Edition p. 365.

coating was obtained under these conditions. The bath showed good throwing power and covering power and the zinc deposited was of a good quality and high ductility.

Considerable hydrogen was liberated throughout the plating operation and consequently the deposit was badly blistered. Approximately 50% of the zinc was blistered and the other 50% (by area) showed very little adhesion to the magnesium.

Variations of current density and temperature within the recommended ranges had no appreciable effects on the character of the deposits obtained.

Although the results obtained by this bath were not very favorable they were good enough to warrant further investigation with cyanide baths.

BRIGHT ZINC BATH

The bright zinc bath is essentially a variation in solution composition of the above cyanide bath, with the additional requirements of brightening and rapid covering agents.

Maintenance of bright type of bath must be carefully controlled in order to insure good cathode efficiency combined with operable bright current density ranges. High purity metals must be used exclusively, since the bright bath is extremely susceptible to exceedingly small amounts of heavy metals or other impurities. The fact has long been recognized that even minute amounts of some metals

effect the physical and chemical properties of zinc metal to a marked degree, and this was likewise found true in bright zinc plating, in which minute amounts of heavy metals markably effect the color and brightness of the deposits. It is believed that molybdenum used as an inorganic brightener in zinc baths, may excercise its effectiveness in sequestering small amounts of lead by combining with it to form a complex compound.(7)

Since the color and brightness of the plate is only of secondary importance, extreme precaution was not necessary in this work.

The applications and value of bright zinc result from its combination of bright appearance and protective value. In many cases bright zinc is now applied even to metal articles not requiring a bright finish but whose sales appeal is thereby augmented. In recent years the control of the bright bath has been simplified, and ample experience now enables accurate predictions as to the applicability in the case of almost all the industrial articles.

It is not the purpose of this paper to describe each bath in detail and for a good description of the bright zinc bath the reader is referred to the works of Co. Hull and C. G. Wernlund.(8)

As previously stated the primary problem to be overcome in plating zinc on magnesium is the poor adhesion,

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(7) Modern Electro-plating (The Electrochemical Society) 1942 Ed. p. 367

(8) Modern Electroplating 1942 Edition p. 359.

probably because of the characteristic formation of the film of magnesium hydroxide on the surface of the metal.

The succeeding investigation deals with a method to improve the adhesion of the zinc by (1) pre-treating methods of magnesium and (2) by variations in the bath compositions.

BATH III.

Bright plating cyanide bath.

$Zn(CN)_2$.....70 g./L.

Na(CN) .....42 g./L.

Na OH .....80 g./L.

$$M = \frac{\text{Total NaCN}}{\text{Zn}} = 2.6$$

$T = 29^0$ C.

Current Density = 2-10 Amps/ dm^2

pH = 11

The first bright deposit was in reality a repetition of the last deposit obtained from the ordinary cyanide bath, since the baths are essentially the same except for the previously mentioned advantages of the bright baths. It could be expected then, that with the same preplating treatment, the same general deposit would be obtained. This proves to be the case. A good deposit was secured at high efficiency but there were an abundance of blisters and little adhesion to the magnesium. Several other cleanning solutions with concentrations of sodium carbonate ranging from 10 - 100 grams/ liter and NaOH from 5 - 50 g/liter

were employed along with dips in various concentrations of HCl and H_2SO_4 without any appreciable effect upon the adhesiveness of the zinc to the magnesium.

At this point it became evident that little or no adhesion could be obtained by any of the conventional methods of treating magnesium prior to plating.

W. S. Loose (9) in his recently developed nickel plating procedure, developed an entirely new pre-plating technique which enabled him to deposit good adhesive nickel plates on magnesium alloys.

The pre-treating steps are as follows:

I. Cathodic cleaning.

BATH

$Na_2CO_3 \cdot 10\ H_2O$	56 g./L.
$Na_3PO_4 \cdot 12\ H_2O$	110 "
Na OH.....	28 "
$Na_2Si\ O_3$.....	56 "
Sodium Lauryl Sulphate.....	7 "

Time 1 minute

Current Density 5.4 Amps/dm^2 ..

Temperature 80° C.

II. Wash with hot water, with cold water.

III. Chrome-pickle etch.

BATH

Chromic anhydride C.P. ($Cr\ O_3$)..120 g./L.

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(9) See Foot-note (1).

Nitric Acid C.P. (HNO_3) ...112 cc./L.

Sulphuric Acid C.P. (H_2SO_4)... 1 cc./L.

Time 5 Seconds

Temperature Room

IV. Wash with cold water.

V. Modifying acid dip.

BATH

Hydrofluoric acid (52% HF).....200 cc./L.

Nitric Acid..... 10 cc./L.

Time 2 - 5 Minutes

Temperature Room

VI. Wash with cold water.

An excellent discussion of these steps is given by Loose who developed this treatment.

After the above treatment the magnesium was plated in the following bath:

BATH

$Zn(CN)_2$.....70 g/liter

Na OH .....80 "

Na CN .....42 "

M = 2, 6

T = 29° C.

Current Density 2 - 10 amp./dm^2

pH = 11

Several deposits were obtained at various current densities within the above range and it was found that with

a current density of one and one-half to two amperes per square decimeter a deposit practically free from blisters was obtained. Also considerable adhesion was obtained although it was not sufficiently good for commercial use.

A high purity carbon anode was substituted for the lead anode and slightly better deposits were obtained. Several tests were run at various temperatures ranging from 20° C. to 40° C. but the character of the deposit dropped off sharply with temperatures outside the established range of 27.8 to 30.6° C.

Apparently the problem of a successful pre-treating technic was solved by the above treatment and the remainder of this investigation was devoted to finding a variation in the bath composition which would give a sufficiently low pH to prevent the formation of the film of magnesium hydroxide on the surface of the magnesium when it was immersed in the solution.

EFFORTS TO LOWER pH

Any change in the concentration of any of the three constituents of the bath necessitates a change in the other two constituents in order to keep the ratio M of total NaCN to zinc within the allowable limits. With M set at 2.3 and the concentration of $Zn(CN)_2$ 60 g./L. the concentration of Na CN and Na OH must necessarily fall within certain limits.

$$M = \frac{\text{Total Na CN}}{\text{Zn}} = 2.3$$

$$\frac{\text{Total Na CN}}{33.4} = 2.3$$

Total NaCN = 76.8 grams

All of the baths with a concentration of NaOH of 7.5 g./L. or more gave a pH value greater than 10.6. According to the facts previously stated, that a film of $Mg(OH)_2$ forms in solutions of higher pH than 10.6, deposits in these solutions would probably not be adherent.

Several deposits were produced and they were substantially the same as those previously produced, thus verifying the above statement.

The deposits obtained from the baths with the concentrations of less than 7.5 grams /liter of Na OH showed some improvements in adhesiveness indicating that the investigation was being conducted satisfactorily. However, because of the high resistance of the bath considerable voltage was necessary which resulted in an abnormally low efficiency. Some efficiencies were found to lie between 10 and 20%. No pH readings were found below 10.5 which would indicate that as soon as the magnesium is immersed in the solution and electrolysis starts the pH would probably rise above the critical value of 10.6 around the cathode due to liberation of hydrogen thus leaving an excess of (OH) ions. Also the hydrogen electrode pH meter used for all pH determinations, is not very accurate for cyanide solutions.

It was evident that the pH could not be substantially reduced by this method and therefore some other system would have to be found.

EFFECT OF SUBSTITUTION OF A NEUTRAL OR SLIGHTLY ALKALINE SALT FOR MOST OF THE Na OH.

In an effort to lower the pH sodium acetate was substituted for various amounts of NaOH. The first bath composition was as follows:

BATH

$Zn(CN)_2$..... 70 g./L.

Na (CN) ..... 42 "

Na AC .....123 "

Na OH ..... 20 "

M = 2.6

T = 29° C.

pH = 10.3

Current density = 6 amps/dm^2

Fast stirring

On the first deposit HCN was detected above the bath and the experiment was discontinued immediately. Probably some hydrogen ions were concentrated around the anode and these in the presence of acetate ions could have reacted with the NaCN to form enough HCN to be noticable.

Lack of time prevented further tests with this bath but in all probability good adherent zinc can be deposited on magnesium and consequently on magnesium alloys with only slight modifications in this bath composition.

STRIPPING OF ZINC DEPOSITS

An effective method for the removal of nickel deposits on magnesium[10] has been successfully applied to the removal of zinc.

The recommended stripping solution contains 25% HF and 5% HNO_3. The magnesium is treated anodically in this bath and zinc goes into solution over a wide range of current densities. Upon being exposed, magnesium completely polorizes due to the formation of MgF_2. When the current drops to zero the magnesium may be withdrawn from the bath, washed in cold water and immediately replaced in the zinc bath.

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(10) See foot-note (1).

CONCLUSIONS AND RECOMMENDATIONS

ADHESION: The adhesion of a deposit to a metal is difficult to measure. There are several tests in use none of which were used on the deposits obtained since the adhesion was not sufficient to warrant any specific test. The deposits obtained from bath three with the Loose pre-treating method however showed much improvement over the previous deposits and it is very probably that with a little more work an adherent zinc deposit can be obtained.

CORROSION RESISTANCE: One of the original purposes of this investigation was to evaluate the corrosive resistance of zinc deposits on magnesium. However, due to limited time and failure to secure a deposit free from blisters and completely adherent, corrosion tests were not attempted.

Magnesium and magnesium alloys are anodic to zinc but the contact potential difference is not very high. Consequently if the zinc deposits were relatively free from porosity magnesium would probably be fairly resistant to corrosion even when in contact with water.

SUMMARY

Magnesium may be readily electroplated with zinc. The best deposits are obtained by, after buffing and cleaning, first dipping in a bath containing 120 grams/liter. CrO_3, 112 cc/liter of HNO_3 and 1 cc/liter of H_2SO_4 for a period of two seconds. After washing, it is dipped in a 10% HF and 1% HNO_3 solution for two minutes. After thorough washing, magnesium can be electroplated in a bath containing 70 grams/liter of $ZnCN_2$, 42 grams /liter of NaCN and 80 grams/liter of Na OH.

The deposit is continuous, soft, and fine grained but is not adherent and contains some blisters. Preliminary work with a modification of this bath containing a considerable quantity of NaAc shows excellent possibilities for producing smooth adherent deposits and certainly warrants further investigation.

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